Bulletin of Electrochemistry 15 (5-6) May-June 1999, pp 183-185

0256-1654/99/$ 3-50

STUDIES ON NEW ELECTROPLATING BATH FOR PLATINUM

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A new platinum plating bath based on $Pt(H_20)_4^{+2}$ complex has been synthesized. The bath is characterized by UV-Visible and electrochemical methods. The plating behavior of the bath was studied as a function of concentration, current densities and *p*H. The results are presented and discussed.

Keywords : UV - Visible, cyclic voltammetry, current efficiency

INTRODUCTION

There is a considerable interest in the development of electroplating baths for platinum, which allow rapid deposition of high quality thick layers [1,2]. Platinum electroplating is usually carried out using P-salt bath, Q-salt bath and DNS salt baths which contain platinum metal in divalent state. The first two bath solutions are prepared from $Pt(NH_3)_2(NO_2)_2$ and $Pt(NH_3)_4^{+2}$ respectively. These baths must operate at *p*H 10 , low current density and elevated temperature for an acceptable current efficiencies and deposit properties. These limitations lead to search for new electroplating systems [3]. In this paper we describe our preliminary studies on plating bath system containing $Pt(H_20)_4^{+2}$ species in 1 *M* perchloric acid medium [3]. The plating bath has been characterized by UV-Visible spectral and electrochemical methods. The efficiency of the bath has been examined. The results are presented and discussed.

EXPERIMENTAL

Synthesis of $Pt(H_20)_4(ClO_4)_2$ complex

The solution containing $Pt(H_20)_4(ClO_4)_2$ in 1 *M* perchloric acid was prepared by known procedures [3,4]. K_2PtCl_4 (1 mM, 0.416 g) was dissolved in 80 ml of 1 *M* perchloric acid and the solution was heated to 340 K. Silver per chlorate (4 mM, 1.0 g) dissolved in 20 ml of 1 *M* perchloric acid was slowly added in portions over period of three hours. After the addition of all silver perchlorate, the solution was left at 353 K for 24 hours with occasional stirring and the light brown precipitate of AgCl was filtered to give yellow solution of $Pt(H_2O)_4(ClO_4)_2$. The volume of the solution was made up to 100 ml, if required, making the concentration of the solution equal to 4 g/l. Any excess Ag^+ ions can be removed by pre-electrolysis at +0.25 V.

Electroplating was carried out in a beaker containing 50 ml of solution. The cathodes were Pt foils (10 mm X 30 mm) which were degreased in trichloroethylene, cleaned in 1 *M* sulfuric acid and finally washed with distilled water. The anodes were large Pt foils. The current efficiency was calculated from weight increase during plating. Cyclic voltammetry was performed on PINE electrochemistry system using model AFRDE 5 bi-potentiostat. Platinum button was used as working electrode. Saturated Calomel Electrode was used as reference and Pt wire as auxiliary electrode. The experiments were carried out under nitrogen atmosphere for the solution concentration of 0.008 *M*. The UV- Visible spectra were recorded on Hitachi U-3400 double beam spectrophotometer.

RESULTS AND DISCUSSION

The solution containing $Pt(H_2O)_4(ClO_4)_2$ was obtained by reacting K_2PtCl_4 with $AgClO_4$ in perchloric acid. The reaction is slow as the ligand substitution at Pt(II) centre is slow [5,6]. However the reaction was completed in 24 hours as evident from the electronic spectrum of the solution. Silver ions react with the liberated chloride ions to form silver chloride precipitate. The completion of the reaction is also evident from the weight of AgCl precipitate. The addition of the $AgClO_4$, should be slow to avoid precipitation $Ag_2[PtCl_4]$ salt. The solution of $Pt(H_2O)_4(ClO_4)_2$ in 1 *M* perchloric acid was examined by UV spectroscopy. The

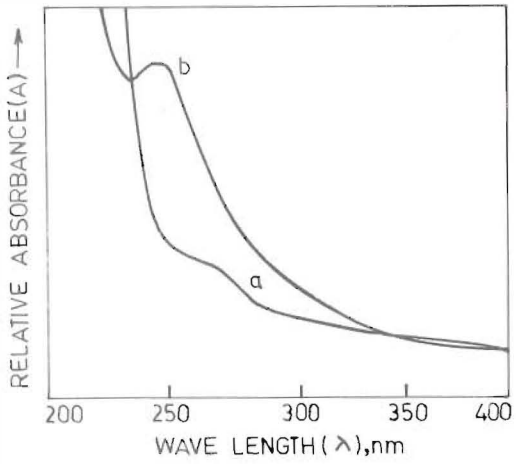

Fig. 1: UV visible spectrum of 0.0001 M a) K_2PtCl_4 b) $Pt(H_2O)_4(ClO_4)_2$ in 1 M perchloric acid

spectrum showed a peak at 270 nm. (Fig. 1) in agreement with literature [4].

The electrochemistry of the complex $Pt(H_2O)_4(ClO_4)_2$ was examined using cyclic voltammetry technique. The complex in 1 *M* perchloric acid exhibited a reduction wave at -0.10 V vs SCE and an oxidation peak at - 0.108 V in the reverse scan at room temperature. The voltammogram is shown in Fig. 2. In the absence of the Pt(II) species the I-E response recorded under the same conditions does not show these redox peaks confirming that the wave at -0.1 V is due to reduction of Pt(II) to Pt(O). This clearly demonstrated the possibility of platinum electroplating at room temperature.

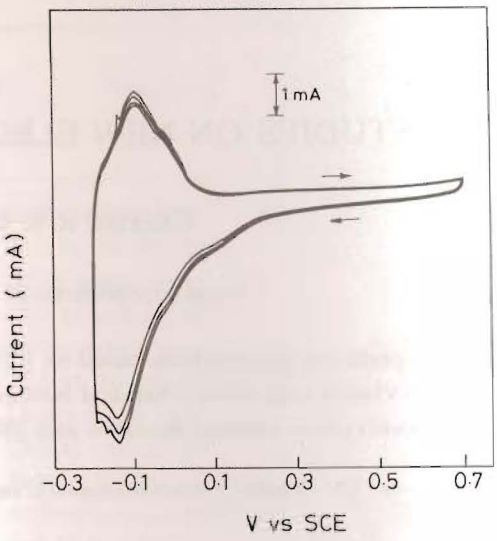

Fig. 2: Cyclic voltammogram of 0.008 M $Pt(H_2O)_4(ClO_4)_2$ in 1 M perchloric acid. The scan rate is 50 mV/sec

As the complex species can be reduced at room temperature, its plating behavior is examined at room temperature. The *p*H of the solution was carefully adjusted to zero by sodium carbonate and the plating was carried out on platinum foils for 30 minutes. The deposit was semibright and adherent. Efficiency was examined as a function of current density, concentration and *p*H of the solution. The data are collected in Table I. One disadvantage of the bath is that it is operated at lower current densities. From the data it is clear that, above a specific value of current density, the coatings are either gray or black non-adherent. The range of the current density

TABLE I: Data on current efficiencies as functions of current density, concentration and *p*H of the platinum plating bath

	*p*H = 0			*p*H = 1		
Concn (g/l)	C.D (mA/cm^2)	Efficiency (%)	Quality of deposit	C.D (mA/cm^2)	Efficiency (%)	Quality of deposit
2	0.25	66.6	Semibright	0.25	89.0	Semibright
	0.50	39.0	Black	0.50	33.0	Black, porous, non adherent
	1.00	20.0	Black, nonadherent	1.00	11.0	Black, porous, non adherent
	1.50	15.0	Black, stripts	1.50	6.0	Black, porous, non adherent
4	0.25	95.5	Semibright	0.25	77.8	Semibright
	0.50	94.5	Semibright	0.50	77.8	Semibright
	1.00	69.5	Gray	1.00	53.0	Black, porous
	1.50	16.5	Black	1.50	15.0	Black, strips, non adherent
6	0.25	89.0	Semibright	0.25	100.0	Semibright
	0.50	89.0	Semibright	0.50	100.0	Black
	1.00	58.0	Gray	1.00	67.0	Black, non adherent
	1.50	30.0	Gray, porous	1.50	19.0	Black, thin film

which gives an acceptable coating increases with increase in concentration of the platinum in the bath. It is also clearly demonstrated that efficiencies of the bath, for all concentrations studied, are significantly improved over the conventional baths. The efficiencies decrease with increase of current density.

The *p*H of the solution was rised to 1.0 and the plating characteristics were examined. The data are indicated in Table I. Black platinum precipitate was formed when the *p*H of the solution was rised to above 2.0 due to disproportionation of Pt(II) species. It was observed that the ageing of the solution occurred at a faster rate for *p*H=1 solution than for *p*H = 0 solution. Thus with increased *p*H, the stability of the complex decreased hence life time of the bath is reduced. It can be generalized from the data that when the *p*H is increased to 1.0, the efficiency is increased only marginally and the range of current densities which give bright coatings are narrowed. At both the *p*Hs studied, use of higher current densites (> 2 mA/cm^2) leads to precipitation of platinum black.

CONCLUSION

A new plating bath for platinum based on $Pt(H_2O)_4^{+2}$, was synthesized and characterized. The results described above show that the reduction of $Pt(H_2O)_4^{+2}$ in 1 *M* perchloric acid to Pt(O) occurs at -0.10 V at room temperature. This observation leads to formulate a new plating bath which gave bright deposits in the *p*H range 0-1.0. Although current densities used were low, increase of platinum concentration in the bath would increase the current density significantly.

REFERENCES

1. M E Baumgartner and Ch J Raub, *Platinum Metals Rev*, **32** (1988) 188
2. P E Skinner, *ibid*, **33** (1989)102
3. A J Gregory, W Levason and D Pletcher, *J Electroanal Chem*, **348** (1993) 211-219
4. L I Elding, *Inorg Chim Acta*, **20** (1976) 65
5. F Basalo and R G Pearson, *Mechanism of inorganic reactions*, Wiley, New York, (1967)
6. R J Cross, *Advances in Inorg Chem*, **34** (1989) 219